

AD-A215 039

AD-A215 039

REPORT DOCUMENTATION PAGE			Form Approved OMB No 0704-0188	
<small>data reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Ave Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.</small>				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 30 Sep 82	3. REPORT TYPE AND DATES COVERED Final (1 Jan 1980)	
4. TITLE AND SUBTITLE PHYSICAL PROPERTIES OF POLYMERS (ULTRASTRUCTURE PROCESSING OF POLYMERS)			5. FUNDING NUMBERS 60012F 2303/A3	
6. AUTHOR(S) Frank E. Karasz			7. PERFORMING ORGANIZATION REPORT NUMBER AFOSR-TR-89-1562	
8. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Massachusetts, Materials Research Laboratory Polymer Science & Engineering Dept Amherst, MA 01003			9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR BLDG 410 BAFB DC 20332-6448	
10. SPONSORING/MONITORING AGENCY REPORT NUMBER AFOSR-80-0101			11. SUPPLEMENTARY NOTES	
12a. DISTRIBUTION/AVAILABILITY STATEMENT All rights reserved; distribution unlimited.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) <div style="text-align: center;">DTIC ELECTE DEC 06 1989 S D CB D</div>				
14. SUBJECT TERMS			15. NUMBER OF PAGES 14	
16. PRICE CODE			17. SECURITY CLASSIFICATION OF REPORT unclassified	
18. SECURITY CLASSIFICATION OF THIS PAGE unclassified			19. SECURITY CLASSIFICATION OF ABSTRACT	
20. LIMITATION OF ABSTRACT				

SPOSR-TR. 89-1562

ACKNOWLEDGEMENT

The Principal Investigator would like to express his sincere thanks to Dr. Donald L. Ball, Director of Chemical Sciences, Air Force Office of Scientific Research, to Dr. Donald R. Ulrich, Program Manager, Directorate of Chemical Sciences, and to other members of the Directorate, for their unfailing cooperation, help and courtesy extended to him during the period of this grant.

Assigned For	
THIS GRANT	<input checked="" type="checkbox"/>
OTHER TASK	<input type="checkbox"/>
PROJECTS	<input type="checkbox"/>
By	
Date	
Signature	
Title	
Unit	
A-1	



CONTENTS

- I. Title
- II. Principal Investigator
- III. Grant Number
- IV. Dates
- V. Senior Research Personnel
- VI. Junior Research Personnel
- VII. Abstract of Accomplishments
- VIII. Description of Research Undertaken
 - A. Polymer Blends
 - B. Plasticization of Network Polymers
 - C. Quasi-Elastic Light Scattering
 - D. Novel Composites
 - E. Ultrastructure
 - a. Synthesis
 - b. Extensional Flow Processing
 - F. Other Investigators
- IX. Publications

- I. TITLE: Physical Properties of Polymers
(Ultrastructure Processing of Polymers)
- II. PRINCIPAL INVESTIGATOR: Dr. Frank E. Karasz
Polymer Science and Engineering
University of Massachusetts
Amherst, Massachusetts 01003
- III. GRANT NUMBER: AFOSR 80-0101
- IV. DATES: 1 January 1980 - 30 September 1982
- V. SENIOR RESEARCH PERSONNEL*: Dr. C. Crosby Dr. G. ten Brinke
Dr. T. Ellis Dr. R. Vukovic
Dr. X. Jin
Dr. Y. Maeda
Dr. M. Miller (MIRP)
- VI. JUNIOR RESEARCH PERSONNEL*: V. Chacko
K. Djordjevic
S. Frederick (MIRP)
J. Schroeder
G. Tostiga (MIRP)
S. Zacharius

*Research Personnel supported through Faculty Associates after
1 October 1981 are indicated by MIRP.

VII. ABSTRACT OF ACCOMPLISHMENTS

This report covers the period January 1, 1980, to September 30, 1982. For the first twenty-one months the research undertaken was an extension of earlier AFOSR supported endeavors dealing mainly with the physical properties of polymer blends, the plasticization of epoxy and other network polymers by water, and the characterization of stiff chain macromolecules by quasi-elastic light scattering. A number of other topics received attention, detailed below. On 1 October 1981 the objectives of AFOSR 80-0101 were expanded; it became a Multiple Investigator Research Project (MIRP) with a new focus for that of producing novel ultrastructural assemblies of macromolecules with electrical properties of interest. Two Faculty Associates, Professors R.W. Lenz and H.H. Winter, both of the Chemical Engineering Department here, were incorporated into the supported research program. However work on the previously identified areas in the physical properties of polymers, carried out by the P.I., was also continued, and is discussed below. The ultrastructural research program was therefore only at a relatively early stage at the conclusion of the time frame covered by this Report.

In the polymer blend research substantial progress was achieved in elucidating thermodynamic and structural factors underlying the phenomenon of miscibility in binary polymer systems. The effects of chemical structure, tacticity, molecular weight, temperature, and their components were investigated by a number of techniques including calorimetry, vapor absorption, inverse gas

chromatography and by the establishment of binary or ternary phase diagrams for appropriate systems. These were typically poly(2,6-dimethyl phenylene oxide) (PPO) and a halogenated styrene polymer or copolymer. By the conclusion of the reporting period a fairly detailed understanding of these effects and some progress towards prediction of new effects, had been obtained.

The study of the plasticization of network polymers was prompted by an earlier study of the effect on water on epoxy resins. It was established that, contrary to some earlier suppositions, the relatively large depression in the glass transitions of epoxies by small amounts of absorbed water, could be accounted for by purely thermodynamic analysis and did not require, in particular, the concept of specific polymer-sorbate interactions. These ideas were extended, with some success, to other chemically cross-linked macromolecules.

The solution properties of the stiff chain macromolecule poly(p-phenylene benzbisthiazole) (PBT) were studied by depolarized forward scattering proton correlation spectroscopy (quasi-elastic light scattering). By this technique the persistence length and other important chain conformational parameters was obtained for the first time.

Other topics investigated include the properties of a novel composite in which ultra high molecular weight polyethylene is covalently bonded to filler particles, the conformational transitions in polypeptide systems and a number of theoretical problems.

As indicated above the MIRP project on ultrastructure was at a relatively early stage of development at the conclusion of this grant. Nevertheless progress had been on the synthesis of block copolymers with electrically active interior blocks and on the special processing achievable with extensional flow dies.

VIII. DESCRIPTION OF RESEARCH ACCOMPLISHED

The research completed during the grant period is divided into the following areas. In most cases, complete details are presented in the referenced publications or preprints (both available from the P.I.).

A. Polymer Blends

To understand the thermodynamic factors involving miscibility requires a knowledge of basic free energy of mixing data for the system. For some combinations of a halogenated polystyrene this was obtained from heat of solution measurements, (1). Other information was derived from dielectric relaxation data, (3,5) and from mechanical measurements, (2). The phase behavior of these polymers was extensively investigated (10,17,23,24,25,27,31,40,43). In general as the fraction of the halogenated styrene in the respective copolymers is increased, the LCST (lower critical solution temperature) decreases. In the case of copolymers of two dissimilar halogenated styrene units a "window of compatibility" appears (see, for example, ref. 25); a quantitative theory to account for this, which is in press (31), can be now used to calculate interaction parameters χ_{ij} , where i, j represent any monomer units within the system.

The significance of this development lies in the predictability of compatibility from the relatively easily determined χ_{ij} 's. This work has resulted in a number of reviews (2,4,9,12) and theoretical papers (13,18,28,36,40). Other systems have also been investigated, including the effect of tacticity in methacrylate polymers (32, and to be submitted). Crystallinity in these systems has been studied (39,44).

B. Plasticization of Network Polymers

The interaction of water was studied with respect to the effect of the diluent on the glass transition temperature, T_g . It is known that for example in epoxy resins relatively small amounts of water produce large depressions in T_g , (6,37). We were able to account for this effect purely in terms of thermodynamic factors ie. without the necessity of invoking "specific interactions". This treatment was extended to other network systems, (16) and theoretically (22). Quadrupole echo deuterium NMR studies (26) have recently confirmed that the water in epoxies is relatively mobile.

C. Quasi-elastic Light Scattering

Dynamic (quasi-elastic) light scattering can be used to characterize macromolecules in terms of size, conformation and, in favorable circumstances, size distribution. A specific form of this technique, forward depolarized scattering, yields rotational relaxation information directly, and is thus of use with respect to anisotropic conformations. In our work, forward depolarized

light scattering was used to measure persistence lengths (a measure of chain stiffness) in poly(p-phenylene benzbisthiazole), (8). The properties of stiff chain polymers in more concentrated regimes was investigated in another study, (42).

D. Novel Composites

The interface between filler particles and a macromolecular matrix plays a key role in determining the mechanical properties of the composite. A novel composite was obtained in which the matrix (ultra high molecular weight polyethylene) was covalently bound to the surface of the filler particles (CaCO_3 ; Al_2O_3). The properties of this system were intensively examined, (14,15,29,33) in a morphological and mechanical property study.

E. Ultrastructure

a. Synthesis

The goal of this investigation has been to prepare block or graft copolymers which will form two distinct phases in the solid state, and in which one of the phases will be electrically conducting and the other not. To achieve this objective, the block or graft copolymers must be initially, at least, fusible or soluble so that well controlled and well characterized two-phase systems can be formed, and the phase structure must be maintained after doping one of the polymers to form the conducting phase.

One of the polymers for the conducting phase, which was selected for our initial study, was poly-2-vinylpyridine, PVP, which can be doped with either

iodine or TCNB. This polymer can be obtained as a "living polymer" by anionic initiators, so AB block copolymers were prepared with both polystyrene, PS, and polybutadiene, PB, as the A blocks, which form the insulating phase and PVP as the B block for the conducting phase.

The diblock copolymers prepared could be solution cast into films that contained well developed two phase systems, which could be clearly seen by electron microscopy after selectively obtaining either the PB phase with osmium tetroxide, OsO₄, or the PVP phase with iodine or methyl iodide. Considerable control including phase inversion can be achieved over the phase morphology by the manner in which the film is obtained, as well as by variation of polymer composition.

A second polymer under investigation, which has the potential of developing on doping conductivities as high as those of doped polyacetylenes, is polyphenylene vinylene, PPV. In all previous investigations described in the literature, this polymer has not been prepared in sufficiently high enough molecular weights from doped films for conductivity studies. However, we have investigated a new polymerization reaction by which we have been able to obtain strong films of the polymer by solution casting and reacting a precursor polymer. These films could be doped with iodine to a metallic-like appearance; the conversion of the precursor film to the PPV film has been quantitatively achieved, and relatively high conductivities were obtained.

b. Extensional Flow Processing

A new technique has been developed for subjecting small polymeric samples to well defined extensional strains. The sample is introduced between two metal plates which are coated with a lubricant fluid. The sample is squeezed when the metal plates are driven together at a prescribed rate. The lubricant reduces the shear stresses in the sample to a level which is negligibly small. The instrument allows for measuring the squeezing force as well as the squeezing rate. Transient equibiaxial extensional viscosities as measured in this new device have been obtained. This is the first time that such an extensional viscosity has ever been measured for a molten polymer. The technique was developed further and is now capable of stretching at high temperatures and at prescribed rates. Preliminary descriptions of the studies described above are in press (34) and will be extensively discussed in papers to be submitted.

F. Other Investigations

Conformational transitions in stiff, hydrogen-bonded, helices in polypeptides were studied with respect to the effect of temperature, solvent composition and isotope substitution ($H \rightarrow D$) (19,30, and to be submitted). A number of the related theoretical questions (38) were already referred to above.

IX. PUBLICATIONS

1. Pure and Appl. Chem. 52, 409 (1980) (with W. MacKnight)
"Heats of Polymer Mixing".
2. Polymer Alloys. II, D. Klempner and K. Frisch, Eds., Plenum Press, New York, (1980) (with J. Fried and W. MacKnight)
"Compatibility and Tensile Properties of PPO Blends".
3. Polymer 21, 488 (1980) (with P. Alexandrovich and W. MacKnight)
"Dielectric Relaxation of Poly(chlorostyrenes) and their Copolymers".
4. Structure and Properties of Amorphous Polymers, A. Walton, Ed., Elsevier Publishing, Amsterdam (1980) (with W. MacKnight)
"Physical Properties of Compatible Polymer Mixtures".
5. J. Macromol. Sci. - Phys. B17, 501 (1980) (with P. Alexandrovich and W. MacKnight)
"Dielectric Studies of Polymer Compatibility: Blends of Polystyrene/Poly-2-Chlorostyrene".
6. Water in Polymers, S. Rowland, Ed., ACS Symposium Series No. 127, Washington, D.C. (1980) (with P. Moy)
"The Interactions of Water with Epoxy Resins".
7. Thermo. Acta. 42, 51 (1980) (with J. Illinger and N. Schneider)
"Modified Sample Pans for Use in a Perkin-Elmer DSC-2".
8. J. Chem. Phys. 75(9), 1 Nov. 1981 (with C.R. Crosby, III, N.C. Ford, Jr., and K.H. Langley)
"Depolarized Dynamic Light Scattering of a Rigid Macromolecule Poly(p-phenylene benzbisthiazole)".
9. Kem. Ind. 31, 193-198 (1982)
"Solid State Transitions in Polymer Blends".
10. Hemi. Ind. (Yugoslavia) 35, 361-363 (1981) (with R. Vukovic and W. MacKnight)
"Compatibility Study of Fluorosubstituted Styrene with Poly(2,6-Dimethyl-1,4-Phenylene Oxide) and with Polystyrene".
11. Thermochemica Acta 54, 349-356 (1982) (with R. Vukovic, V. Kuresevic, and W.J. MacKnight)
"The Investigation of the Compatibility and Phase Separation of Poly(2,6-Dimethyl-1,4-Phenylene Oxide) and Styrene-fluorosubstituted Styrene Copolymer Blends by Differential Scanning Calorimetry".

12. Polymer Compatibility, K. Solc, Ed., MMI Press, Midland, Michigan (1982), p. 165-175 (with W.J. MacKnight)
"Solid State Properties of Polymer Blends".
13. J. Chem. Phys. 77(10), 5249-5250 (1982) (with G. ten Brinke)
"Scaling Theory and Enthalpy of Mixing for Binary Fluids".
14. Polym. Eng. Sci. 22, 968-974 (1982) (with V.P. Chacko and R.J. Farris)
"Dynamic Mechanical Behavior of Filled Polyethylenes and Model Composites".
15. J. Polym. Sci. 20, 2177-2195 (1982) (with V.P. Chacko, R.J. Farris, and E.L. Thomas)
"Morphology of CaCO₃-Filled Polyethylenes".
16. J. Appl. Polym. Sci. 28, 23-32 (1983) (with T.S. Ellis and G. ten Brinke)
"The Influence of Thermal Properties on the Glass Transition Temperature in Styrene/Divinylbenzene Network-Diluent Systems".
17. J. Appl. Polym. Sci. 28, 219-224 (1983) (with R. Vukovic and W.J. MacKnight)
"Compatibility of Some Fluorosubstituted Styrene Polymers and Copolymers in Blends with Poly(2,6-Dimethyl-1,4-Phenylene Oxide) and with Polystyrene".
18. J. Chem. Phys. 78, 995-996 (1983) (with G. ten Brinke)
"An Improved Upper Bound for the Free Energy of a Single Chain Lattice Model".
19. Int. J. Biol. Macromol. 5, 53-56 (1983) (with G.E. Gajnos and D.C. Lu)
"Conformational Stability of Deuterated Poly(B-Benzyl-L-Aspartate) in m-Cresol".
20. S. Zacharius, Ph.D. Thesis, University of Massachusetts (1982).
21. J. Material Sci. 18, 721-729 (1983) (with R.K. Galkiewicz)
"Viscoelastic Characterization of Poly(Butylene Terephthalate) using Longitudinal Resonances".
22. Macromolecules 16, 244-249 (1983) (with G. ten Brinke and T.S. Ellis)
"Depression of Glass Transition Temperature of Polymer Networks by Diluents".
23. J. Appl. Polym. Sci. 28, 1379-1389 (1983) (with R. Vukovic, V. Kuresevic, N. Segudovic, and W.J. MacKnight)
"Compatibility of Poly(2,6-Dimethyl-1,4-Phenylene Oxide)/Poly(Fluorostyrene-Co-Chlorostyrene) Blends".

24. *Macromolecules* **16**, 381-387 (1983) (with S.L. Zacharius, G. ten Brinke, and W.J. MacKnight)
"Evidence for Critical Double Points in Blends of Polystyrene and Poly(o-chlorostyrene)".
25. *Polymer* **24**, 529-533 (1983) (with R. Vukovic and W.J. MacKnight)
"Compatibility of Poly(p-fluorostyrene-co-o-fluorostyrene) with Poly(2,6-dimethyl-1,4-phenylene oxide) and Polystyrene".
26. *Macromolecules* **16**, 1019 (1983) (with L.W. Jelinski, J.J. Dumais, R.E. Stark, and T.S. Ellis)
"The Interaction of Epoxy Resins with Water: A Quadrupole Echo Deuterium NMR Study".
27. *J. Polym. Alloys*, (in press)
"Thermally Induced Phase Separation in PPO Blends".
28. *J. Chem. Phys.*, (in press)
"Scaling Theory, Volume of Mixing and Effect of Pressure".
29. V. Chacko, Ph.D. Thesis, University of Massachusetts, 1982.
30. *Biopolymers*, (in press)
"Heat Capacity Increments: Conformational Transitions in Polypeptides".
31. *Macromolecules*, (in press)
"Phase Behavior in Copolymer Blends: Poly(2,6-Dimethyl-1,4-Phenylene Oxide) and Halogen-Substituted Styrene Copolymers".
32. J. Schroeder, Ph.D. Thesis, University of Massachusetts, 1982.
33. *J. Appl. Polym. Sci.*, (in press)
"Tensile Properties of CaCO₃ Filled Polyethylene".
34. *Ultrastructure*, (in press)
"Ordered Block Copolymers".
35. *Analytical Calorimetry*, (in press)
"The Effect of Sample Temperature Gradients on DSC Thermograms at the Glass Transition Temperature".
36. *Macromolecules*, (in press)
"Semi-Flexible Directed Self-Avoiding Walks".
37. *Polymer*, (in press)
"The Interaction of Epoxy Resins with Water: The Depression of Glass Transition Temperature".

38. J. Chem. Phys., (in press)
"The One-Dimensional $n \rightarrow o$ Vector Model and the Helix-Coil Transition".
39. Macromolecules, (in press)
"Equilibrium Melting Point Depression for Blends of Isotactic Polystyrene with Poly(2,6-Dimethyl Phenylene Oxide)".
40. Macromolecules, (in press)
"LCST Behavior in Polymer Blends: Compressibility and Directional Specific Interactions".
41. Macromolecules, (in press)
"Comment on the Correct Polarization Factor for Light Scattering Photometers Employing Annular Detection".
42. Macromolecules, (in press)
"Dynamic Light Scattering Study of Semidilute Solutions of a Stiff Chain Polymer".
43. Adv. in Chem. Series, (in press)
"A Polymer Blend Exhibiting Both Upper and Lower Critical Solution Temperature Behavior: Polystyrene/Poly(Orthochlorostyrene)".
44. J. Polym. Sci., Phys. Ed., (in press)
"Water Induced T_g Depression in Nylon 6".
45. Macromolecules, (in press)
"On the Kinetic Delay for the Melting of Polymer Crystals".